

The
Condensation of Nitromalonic
Aldehyde

With Certain Diketones

BY
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The Condensation of Nitromalonic Aldehyde

With Certain Diketones

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The author wishes to express his indebtedness to Professor William J. Hale for the constant interest which he has shown during the course of this research.

CONTENTS

I. HISTORY.

Occurrence and Physical Properties of Cyclopentadiene....	7
Synthesis of Cyclopentadiene Derivatives	8
Reactions of Cyclopentadiene and Its Derivatives:	
<i>a</i> Reactions of Addition	10
<i>b</i> Reactions involving the Methylene Hydrogen.....	12

II. THEORETICAL CONSIDERATIONS.

Introduction	14
Condensation of Diphenacyl and Nitromalonic Aldehyde....	15
Constitution of Condensation Product.....	16
Derivatives of 2, 3-Dibenzoyl-5-Nitrocyclopentadiene.....	17
Influence of Negative Substituents upon Character of Ethylene Linking	18
Monobromdiphenacyl	19
Dibromdiphenacyl	20
Effect of Substituents in Benzene Nucleus of Diphenacyl upon the Rate of Condensation.....	21

III. EXPERIMENTAL PART.

Diphenacyl and Nitromalonic Aldehyde:	
Preparation of Materials	22
2, 3-Dibenzoyl-5-Nitrocyclopentadiene	23
Sodium Salt of "	23
Barium Salt of "	24
Silver Salt of "	24
Monoxime of "	24
Monophenyl-hydrazone of "	25
7-Nitro-1, 2, 4-triphenylcyclopentadio-dihydropyridazine....	26

Anil fo 2, 3-Dibenzoyl-5-Nitrocyclopentadiene.	27
Oxidation of 2, 3-Dibenzoyl-5-Nitrocyclopentadiene:	
<i>a</i> With Nitric Acid	27
<i>b</i> With Potassium Permanganate	28
Behavior of 2, 3-Dibenzoyl-5-Nitrocyclopentadiene towards	
Reducing Agents	29
Para-Dimethyldiphenacyl and Nitromalonic Aldehyde:	
Para-dimethyldiphenacyl	29
2, 3-Para-ditoluyl-5-Nitrocyclopentadiene	29
Silver Salt of "	30
Monoxime of "	31
4-Bromdiphenacyl and Nitromalonic Aldehyde:	
Para-bromacetophenone	31
Preparation of Brombenzene	32
Para-bromphenacyl Bromide	33
Para-bromphenacyl Benzoylacetic Ester	33
Para-bromdiphenacyl	34
2-Parabrombenzoyl-3-benzoyl-5-nitrocyclopentadiene	35
7-Nitro-1, 2-diphenyl-4-parabromphenyl-cyclopentadio-	
dihydropyridazine	36
4, 4'-Dibromphenacyl and Nitromalonic Aldehyde:	
Para-brombenzoic Acid	36
Para-brombenzoyl Chloride	37
Sodium Salt of Parabrombenzoyl-acetoacetic Ester.	38
Para-brombenzoylacetic Ethyl Ester	38
Dehydro-parabrombenzoylacetic Acid	39
Para-bromphenacyl-parabrombenzoylacetic Ethyl Ester.	39
4, 4'-Dibromdiphenacyl	40
2, 3-Para-dibromdibenzoyl-5-nitrocyclopentadiene.	41
Summary	42

A. OCCURRENCE AND PHYSICAL PROPERTIES OF CYCLOPENTADIENE

In 1885 Roscoe,¹ while investigating the most volatile portions of the hydrocarbons resulting from the decomposition of crude phenol at a red heat, isolated a crystalline substance of the formula $C_{10}H_{12}$. He showed that the hydrocarbon decomposed when distilled at ordinary pressure, but at 9 mm. pressure it came over at 63° . When heated in a vacuum-tube at 180° the substance underwent polymerization. To trace the genesis of the hydrocarbon, Roscoe distilled a large quantity of the first runnings from coal tar. When the fraction boiling below 30° was redistilled, after having remained in a sealed tube for several weeks, about thirty percent of it came over above 30° , and a solid crystalline residue remained in the flask. This proved to be identical with the hydrocarbon obtained from the crude phenol. It appeared, then, that these volatile hydrocarbons polymerize spontaneously at the ordinary temperature and that the solid $C_{10}H_{12}$ is probably the final product. Although unable to separate the volatile hydrocarbon which yielded the polymer, Roscoe believed the latter to result from a hydrocarbon C_5H_6 .

Krämer and Spilker,² in an article dealing with the isolation of indene and styrole from coal tar, expressed the hope of finding in the most volatile portions of coal tar the hydrocarbon C_5H_6 closely related to indene and fluorene.

Etard and Lambert³ found this hydrocarbon in petroleum oil. After repeated fractionation they obtained a hydrocarbon C_5H_6 which boiled at 42.5° and which they called pyropentylene. It polymerized readily, as Roscoe had already found, and this dipyropentylene dissociated, upon being heated, into the original pyropentylene.

A few years later Krämer and Spilker⁴ undertook to establish the constitution of the hydrocarbon C_5H_6 . In view of the fact that the substance was capable of taking up four atoms of bro-

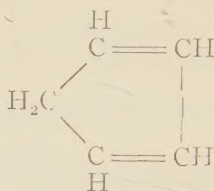
¹ J. Chem. Soc. 47, 669 (1885); Ann. 232, 348 (1886).

² Ber. 23, 3283 (1890).

³ Comp. rend. 112, 945 (1891).

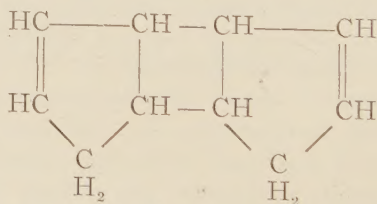
⁴ Ber. 29, 552 (1896).

mine or chlorine they assigned the following structural formula to the compound and called it cyclopentadiene.



According to Étard and Lambert⁵ cyclopentadiene is a liquid having a specific gravity 0.803 and a boiling point of 42.5°. They describe the substance as having a taste resembling pepper and a peculiar odor. Krämer and Spilker⁶ give the boiling point as 41° and the specific gravity 15°/15° as 0.815. It is insoluble in water but miscible with alcohol, ether or benzene in all proportions. The molecular dispersion, as found by Auwers and Eisenlohr⁷ agrees well with the theoretical value (0.87) calculated from the formula. The molecular refraction and molecular volume have been determined by Eijkman.⁸

As indicated above cyclopentadiene shows a great tendency to polymerize to a substance of empirical formula $\text{C}_{10}\text{H}_{12}$, and this latter, upon being heated, dissociates into the original hydrocarbon. To the polymeric form Krämer and Spilker assign the following constitution:



B. SYNTHESIS OF CYCLOPENTADIENE DERIVATIVES.

Duden and Freytag⁹ have found that, under the influence of

⁵ Loc. cit.

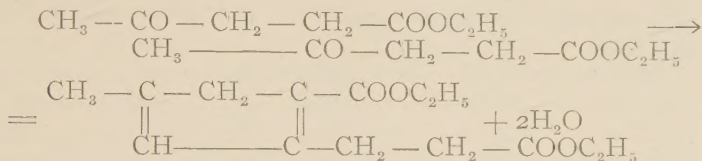
⁶ Loc. cit.

⁷ Ber. 43, 1545 (1910).

⁸ Chem. Zentr. 1907, II, 1211.

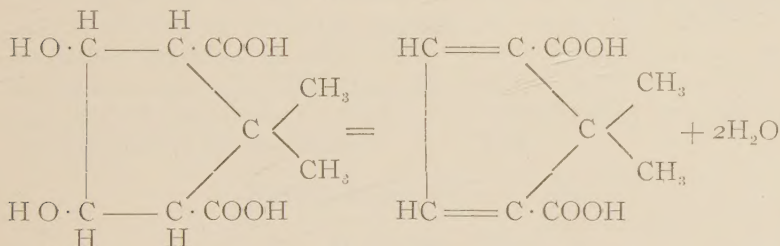
⁹ Ber. 36, 944 (1903).

sodium ethylate, two molecules of levulinic ethyl ester condense to a carboxylic acid derivative:

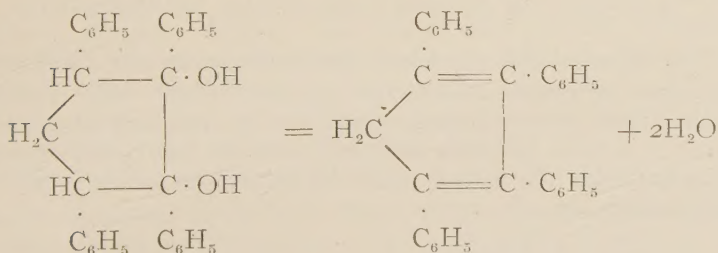


Upon being heated at atmospheric pressure the free acid loses two molecules of carbon dioxide, forming 4-methyl-2-ethyl-cyclopentadiene. By heating the acid in vacuo at 220° it is possible to split off only one carbon dioxide, the resulting product being 4-methyl-1-carbethoxyl-cyclopentadiene-2-propionic acid.

Komppa¹⁰ obtained 5, 5-dimethyl-1, 4-dicarboxy-cyclopentadiene upon heating dioxo-apocamphoric acid:



A triphenyl¹¹ and also a tetraphenyl-cyclopentadiene¹² have been prepared from triphenyl-dihydroxycyclopentane and tetraphenyl-dihydroxypentane respectively by the action of alcoholic hydrogen chloride.¹³



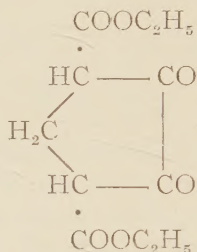
¹⁰ Ber. 34, 2472 (1901).

¹¹ Ann. 302, 236 (1898).

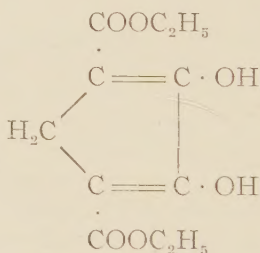
¹² Ann. 302, 233 (1898).

¹³ Ber. 36, 933 (1903).

Dieckmann¹⁴ has shown that oxalic ester in the presence of sodium ethylate condenses with glutaric ester with the formation of a carbocyclic compound, to which he at first assigned a ketonic structure:



In view of the acidic properties of the substance he later took the view that its behavior was more adequately represented by an enolic form:



This hydroxycyclopentadiene derivative has the properties of a strong acid: its water-alcohol solution reddens blue litmus, and it is easily dissolved by a solution of sodium acetate.

C. REACTIONS OF CYCLOPENTADIENE AND ITS DERIVATIVES.

The chemical changes which this hydrocarbon and its derivatives may be caused to undergo are divisible into two general classes: first, those reactions which concern the addition of elements or radicals to one or both of the double bonds, and second, those in which the hydrogen of the methylene group is immediately involved.

a. Reactions of Addition.

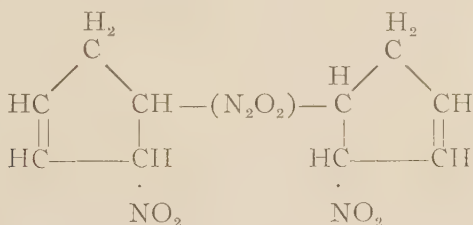
It has already been pointed out that the ability of cyclopentadiene to add four atoms of bromine gave Krämer and Spil-

¹⁴ Ber. 27, 965 (1894); *ibid.* 32, 1931 (1899); *ibid.* 35, 3201 (1902).

ker a clue to the constitution of the hydrocarbon. The same investigators were able to prepare also a solid dibromide. Thiele¹⁵ has studied the subject more fully. In addition to the solid dibromide of Krämer and Spilker, Thiele obtained a liquid dibromide which is formed at the same time. This latter product he called the cis-cyclopentadiene dibromide. On oxidation with dilute potassium permanganate at 0° it gave cis-1, 4-dibrom-2, 3-dioxy-cyclopentane, with a melting point of 78°. With chromic acid this latter substance yielded inactive α , γ -dibromglutaric acid. By similar treatment the solid dibromide or "trans" modification was converted into trans-1, 4-dibrom-1, 3-dioxycyclopentane and racemic α , γ -dibromglutaric acid.

Étard and Lambert¹⁶ found that cyclopentadiene, when shaken with an aqueous solution of sulfur dioxide, yielded a crystalline compound of the empirical formula $C_{10}H_{12} \cdot 2H_2SO_3$.

Wieland and Stenzel¹⁷ passed a current of nitrous anhydride into a solution of cyclopentadiene in dry ether and obtained a crystalline addition product which readily polymerized to an amorphous substance. When in an impure condition, the addition product may be easily exploded. The following constitution was assigned to the compound:



Cyclopentadiene behaves like certain of the terpenes towards nitrosyl chloride. Krämer and Spilker were the first to investigate this addition reaction which was more fully studied by Wieland.¹⁸ The latter showed that chlor-amino-dihydro-dicyclopentadiene was formed in the reduction of the nitrosochloride by means of zinc and alcoholic hydrogen chloride.

Contemporaneously with Wieland, Rule¹⁹ investigated the action of nitrosyl bromide on the cyclopentadienes. He obtained a dicyclopentadiene nitrosobromide by the action of amyl nitrite

¹⁵ Ann. 314, 296 (1901).

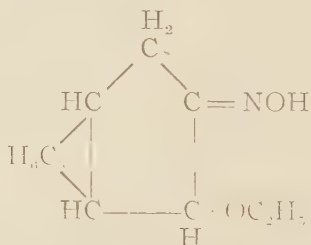
¹⁶ Loc. cit.

¹⁷ Ann 360, 299 (1906).

¹⁸ Ber. 39, 1492 (1906).

¹⁹ J. Chem. Soc. 89, 1339 (1906).

and fifty percent hydrobromic acid on dicyclopentadiene dissolved in acetic acid. This nitrosobromide is much more stable than the monocyclopentadiene nitrosobromide. When the latter is heated with an excess of sodium ethylate solution an oxime derivative, ethoxy-isonitroso-dicyclopentadiene, is formed:



Staudinger²⁰ has shown that cyclopentadiene adds one molecule of diphenylketene, giving a white crystalline substance melting at 89°-90°. A similar behavior has been noticed by Albrecht²¹ in the case of cyclopentadiene and quinones of the type of benzoquinone and α -naphthoquinone. When heated both classes of compounds are resolved into their components.

Cyclopentadiene is a strong reducing agent, ammoniacal silver nitrate being quickly reduced to metallic silver. Eijkman,²² employing the method of Sabatier and Sendersens, reduced the hydrocarbon to cyclopentane.

b. Reactions involving the methylenic hydrogen.

The hydrogen atoms of the methylene group in the cyclopentadiene nucleus are capable of entering into a variety of reactions which find a parallel in the case of compounds of the type of malonic ester and acetoacetic ester. This activating influence, due to the presence of the double bonds, does not, however, appear as pronounced as that occasioned by the presence of the carbonyl groups in the class of compounds just mentioned. Thus Thiele²³ found that cyclopentadiene condenses with ethyl nitrite, in the presence of sodium ethylate, giving the sodium salt of isonitrosocyclopentadiene. With ethyl nitrate, under the same conditions, the intensely colored sodium salt of an unstable nitro body is formed. In similar manner ethyl oxalate with the same condensing agent gave an orange red sodium salt of cyclopen-

²⁰ Ber. 40, 1145 (1907); Ann 356, 94 (1907).

²¹ Ann. 348, 31 (1906).

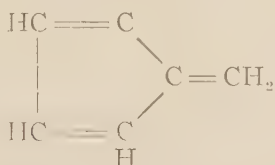
²² Chem. Zentr. 1903, II, 989.

²³ Ber. 33, 666 (1900); Ann. 348, 1 (1906).

tadiene oxalic ester. This latter substance, as well as the nitro derivative, was found capable of reacting with diazonium salts, while cyclopentadiene itself with benzene diazonium chloride, in the presence of sodium acetate, gives cyclopentadiene azobenzene,²⁴ a substance crystallizing in brown leaflets and melting at 130°.

Cyclopentadiene is capable of forming salts under certain conditions. Thus, when the hydrocarbon in benzene solution is treated with the metal, there is formed the yellow potassium salt,²⁵ a substance spontaneously inflammable in contact with the air. Carbon dioxide, acting upon the potassium salt, converts the latter into a salt of bis-cyclopentadiene dicarboxylic acid. Compounds with salts of the heavy metals are known. Thus Holmann and Seiler²⁶ treated dicyclopentadiene with an alcoholic solution of mercuric chloride and obtained a derivative of the empirical formula $\text{Cl} - \text{Hg} - \text{C}_{10}\text{H}_{12} - \text{OC}_2\text{H}_5$.

Cyclopentadiene condenses readily with aldehydes and ketones under the influence of sodium hydroxide or sodium ethylate. Thiele²⁷ called this class of compounds fulvenes, and assigned to the parent substance, which is derived from formaldehyde, the following constitution:



The brilliant color of the compounds in this series is accounted for by the atomic configuration in this formula, the similarity to the atomic arrangement of benzoquinone being at once noticeable. The stability of the substances as a class is not very great, although the fulvenes derived from ketones are, as a rule, somewhat more resistant towards oxidizing agents than the products from aldehyde condensations. Dimethyl fulvene, from acetone, is an orange colored oil boiling at 46° under 11 mm. pressure. It quickly takes up oxygen from the air, being in part resinified and forming a diperoxide,²⁸ $\text{C}_8\text{H}_{10}\text{O}_4$, which explodes violently when heated to 130°.

²⁴ Ber. 39, 2022 (1906).

²⁵ Ber. 34, 68 (1901).

²⁶ Ber. 39, 3187 (1906).

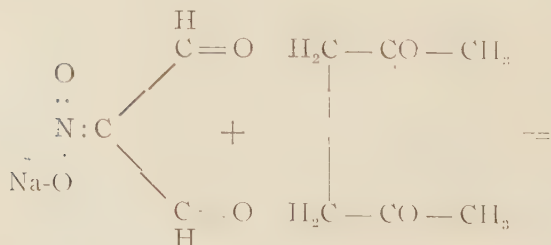
²⁷ Ber. 33, 666 (1900); Ann. 348, 1 (1906).

²⁸ Ber. 34, 2933 (1901).

II. THEORETICAL CONSIDERATIONS

It has been shown by Hill¹ and his co-workers² that compounds of the aromatic series are the principal products resulting from the condensation of acetone, or certain of its derivatives, with nitromalonic aldehyde. With acetone, itself, it is probable that the first product of the reaction is a dihydrobenzene, which, through a molecular rearrangement, is transformed into para-nitrophenol. In the same way, nitromalonic aldehyde and acetoacetic ester gave 5-nitro-salicylic acid, while with benzyl-methyl ketone 5-nitro-2-hydroxydiphenyl was formed.

Hale and Robertson³ have shown that the reaction between nitromalonic aldehyde and acetonylacetone gives rise to 2-acetonyl-4-nitrophenol, which, through the action of a second molecule of the dialdehyde upon the acetonyl group, is transformed into a diphenyl derivative. In this paper the authors state that the acetonyl-nitro-phenol is not, however, the only product of the reaction, a second substance of an entirely different nature being formed in much larger quantity. Hale and Robertson did not attempt to establish the constitution of this latter body; but Hale⁴ has recently shown that it is to be considered as a carbocyclic compound: 2, 3-diacetyl-5-nitro-cyclopentadiene, and he explains its formation by the following equation:

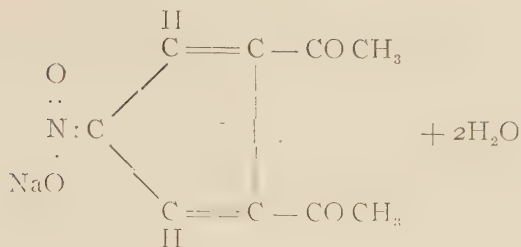


¹ Amer. Chem. J. 22, 89 (1899).

² Ibid., 24, 1 (1900); 33, 1 (1905).

³ Amer. Chem. J., 39, 680 (1908).

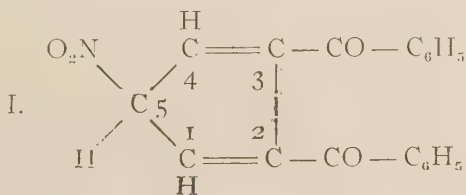
⁴ Ber. 45, 1596 (1912).



If this view be the correct one, it should be possible to involve in condensation with nitromalonic aldehyde the two adjacent methylene groups of a substance, having a constitution analogous to acetonylacetone, and at the same time without the methyl, or any other group, capable of entering into reaction with nitromalonic aldehyde. Such a compound is symmetrical dibenzoyl ethane, or diphenacyl, and the subject of this work is a study of the condensation of this ketone with nitromalonic aldehyde.

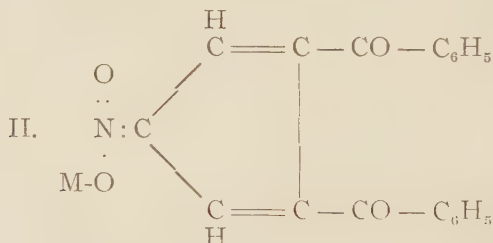
Because of the miscibility of acetonylacetone with water or alcohol, a direct comparison of the ease of condensation of acetonylacetone and of diphenacyl with nitromalonic aldehyde is not feasible. It was thought, however, that some idea of the influence, if pronounced, of the acyl radical in the diketone might be gained through a study of the condensation of certain derivatives of diphenacyl.

The reaction between nitromalonic aldehyde and diphenacyl, in dilute alcoholic solution, in the presence of sodium hydroxide as a condensing agent, was first investigated. At room temperature the reaction was found to proceed rather slowly, and at a temperature of 40° about a week was required for the completion of the condensation. The course of the reaction may be followed by the progressive solubility of the diketone and the deepening red color of the solution. When the diphenacyl has gone completely into solution, the reaction may be considered to have gone to completion. Upon acidification, the solution deposits the condensation product as a yellow precipitate, to which the following constitution is assigned:



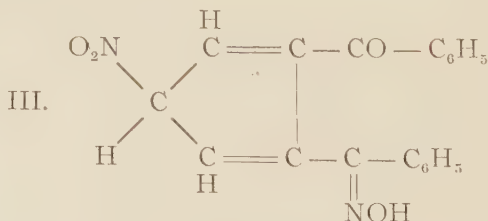
To substantiate this view as to the constitution of the substance, its oxidation was studied. With nitric acid, and also with potassium permanganate, the products were carbon dioxide, oxalic acid and benzoic acid; with the latter oxidizing agent approximately three molecules of carbon dioxide, one molecule of oxalic acid and two of benzoic acid being formed. The nitro group, in the permanganate oxidation, was eliminated, in part, at least, as nitric acid.

The cyclopentadiene derivative contains a nitro group and should, like nitromethane, have a hydrogen atom replaceable by metals. Such was actually found to be the case; salts of the alkalis, alkaline earths and heavy metals being readily formed, and having the following structure:



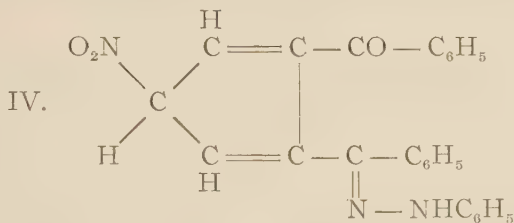
This ease of salt formation may be attributed not only to the presence of the nitro group but also to the influence of the double bonds.

The presence of at least one carbonyl group was proved by the formation of a monoxime. It was found impossible to prepare a dioxime: even with a large excess of hydroxylamine the monoxime was the sole product; this behavior may in part be due to steric hindrance.

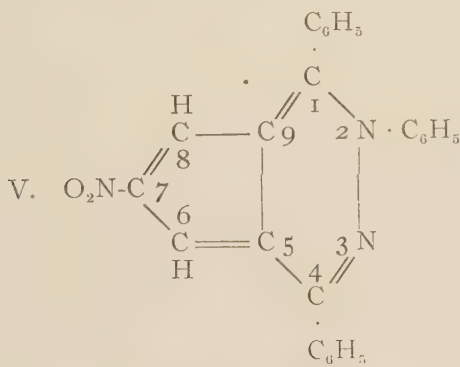


With phenylhydrazine it is possible to involve both carbonyl groups in reaction, not, however, with the formation of a diphenylhydrazone. When the cyclopentadiene, dissolved in an excess of sodium hydroxide, is treated with a warm solution of phenyl-

hydrazine hydrochloride the yellow phenylhydrazone is precipitated in a short time.

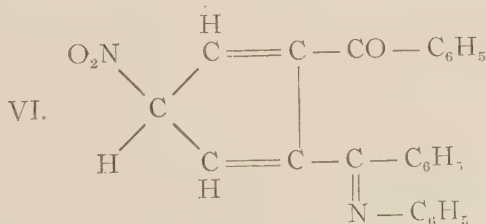


When the phenylhydrazone is heated, or when its alcohol or benzene solution is warmed, it is rapidly transformed into a pyridazine derivative of a deep red color.



Unlike the phenylhydrazone, the pyridazine derivative is insoluble in a solution of sodium hydroxide. This behavior is accounted for on the assumption of a shifting of the double bonds in the cyclopentadiene nucleus. As the formula indicates, the carbon atom carrying the nitro group no longer has a hydrogen atom replaceable by metals.

With aniline the dibenzoyl-nitrocyclopentadiene yields a monanil of the following constitution:



Just as with hydroxylamine, so with aniline it was found that only one of the carbonyl groups was capable of entering into reaction.

In marked contrast to the great tendency of cyclopentadiene itself to form a variety of addition products is the behavior of our condensation products towards those reagents which are ordinarily used to prove the presence of ethylene double bonds. Neither with bromine, nitrosyl chloride, the halogen acids nor with quinone, was there any evidence of a tendency to form an addition product. We attribute this behavior to the strongly negative influence of the substituents in the cyclopentadiene nucleus, an analogous phenomenon having been observed by Hale in the case of the diacetyl-nitrocyclopentadiene, and by Newmann⁵ with triphenylcyclopentadiene. Moreover, Wieland and Stenzel⁶ have recently pointed out that the introduction of two phenyl groups into butadiene so alters the character of the double bonds that diphenyl butadiene, in view of its behavior, may be classed with the aromatic compounds.

The relative effects of various negative groups in suppressing the tendency of ethylene derivatives to form addition products has been more fully investigated by Sudborough and Thomas⁷ and by Hugo Bauer.⁸ The latter has shown that the inhibitive effect produced by the presence of the radical "CN" is greater than that produced by " COOC_2H_5 ", while the effect due to the presence of the " C_6H_5 " group is less than that of either of the other two.

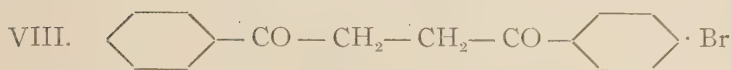
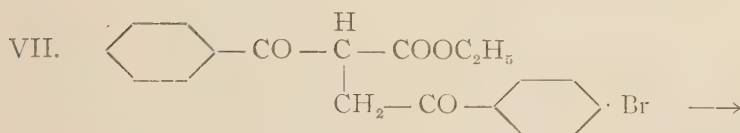
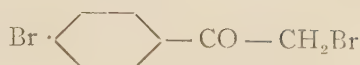
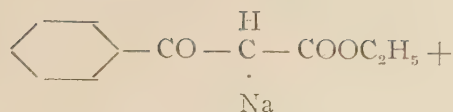
To ascertain whether substituents in the benzene nucleus of diphenacyl had any marked influence upon the ease of condensation with nitromalonic aldehyde, the following derivatives were prepared: 4, 4'-dimethyl-, 4-brom- and 4-4'-dibrom-diphenacyl. The first of these is described in the literature, but for the latter two, methods of preparation had to be devised. The monobrom compound was obtained through the following series of reactions: 1^o, 4-dibromacetophenone with the sodium salt of benzoylactic ester gave para-bromphenacyl benzoylactic ester, which upon treatment with a solution of potassium hydroxide yielded the desired diketone.

⁵ Ann. 302, 236 (1898).

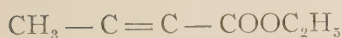
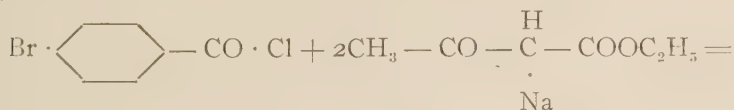
⁶ Ann. 360, 306 (1908).

⁷ J. Chem. Soc. 97, 715, 2450 (1910).

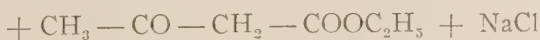
⁸ Jour. pr. Chem. (2) 72, 201 (1905).

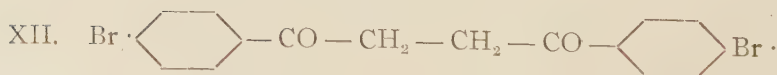
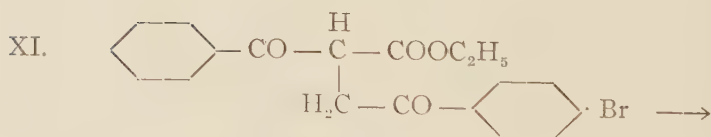
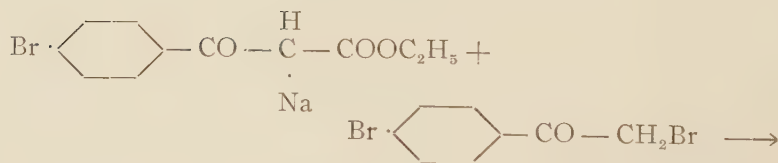
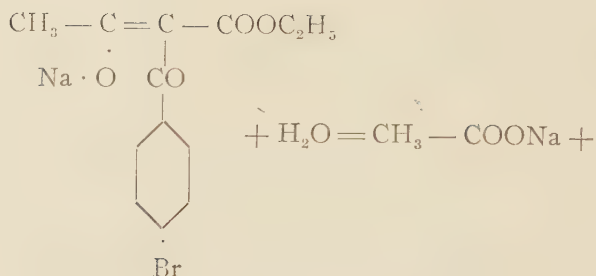


Below is given the procedure which was worked out for the preparation of the dibromdiphenacyl. By the action of para brombenzoyl chloride upon sodium acetoacetic ester the sodium salt of para-brombenzoyl acetoacetic ester was formed. Upon treatment with ten percent ammonia the sodium salt was changed to para-brombenzoyl acetic ester. This ester forms a sodium salt from which parabromphenacyl-parabrombenzoyl acetic ester was prepared by the action of 1², 4-dibromacetophenone. Upon saponification with potassium hydroxide the substituted para-brombenzoyl acetic ester was converted into 4, 4'-dibromdiphenacyl



IX.





The condensation of these derivatives was carried out under conditions as nearly as possible the same as those that obtained in the condensation of diphenacyl itself. The solutions consisted of three parts of 95 percent alcohol and one part water, the total volume of the mixture being in each case proportional to the weight of sodium hydroxide and nitromalonic aldehyde required. The temperature was maintained throughout at 40°. The results are tabulated below:

	Diphenacyl	Monobromdiphenacyl	Dibromdiphenacyl	Dimethyldiphenacyl
Alcohol (c.c.)	75	45	36	45
Water (c.c.)	25	15	12	15
NaOH (2 mols) (grams).....	0.8	0.5	0.4	0.5
Diketone (grams)	2.4	2.0	2.0	1.6
Nitromalonic aldehyde (grams)...	1.6	1.0	0.8	1.0
Approx. sol. (grams per 1000 c.c.)	0.8	0.7	0.1	0.5
Time (days)	10	5	14	14
Conversion	100%	100%	40%	75%

Comparing diphenacyl and the monobrom derivative, whose solubilities are of the same order, it will be observed that the time required for the condensation of the bromdiphenacyl is just one-half that necessary for the conversion of the parent substance. Although the solubility of dimethyldiphenacyl is only slightly less than that of the monobrom derivative, the time required to effect its condensation is about three times as great. In the case of the dibromdiphenacyl it does not appear safe to draw any very definite conclusions. It must be remembered that we are dealing here with an almost insoluble substance, and that this factor must have a pronounced influence upon the rate of condensation. Judging from the behavior of the monobrom and the dimethyl derivatives in relation to the parent substance it may be said that the presence of negative substituents in the benzene nucleus has a tendency to increase the activity of the methylene groups in diphenacyl towards nitromalonic aldehyde.

III. EXPERIMENTAL PART

The nitromalonic aldehyde used in this work was prepared according to the directions of Hill and Torrey,¹ and the diphenacyl after the methods of Knorr² and Fritz.³ In accordance with the method of Knorr, 45 grams of benzoylacetic ester, dissolved in 600 cc. absolute ether, were treated with 5.4 grams of metallic sodium in the form of thin shavings. The mixture was allowed to stand for twenty-four hours with frequent shaking. When particles of sodium were no longer visible and the evolution of hydrogen had ceased, a concentrated ether solution of 27 grams of iodine was added in small portions, the mixture being shaken after each addition. Water was then added to dissolve the sodium iodide and the slight excess of iodine removed by a solution of sulphurous acid. The ether phase was separated and, after the distillation of the ether, the residual dibenzoyl succinic ester was recrystallized from ninety percent alcohol. Yield, 24 grams.

Twenty-four grams of dibenzoyl succinic ester were heated on the water bath with a solution of 10 grams of sodium hydroxide in 330 cc. of water. After about five hours the saponification was complete and the diphenacyl had separated as a flocculent precipitate. After one recrystallization from ninety-five percent alcohol a pure product, melting at 145° , was obtained. Yield 5 grams.

In order to prepare the diketone by the method of Fritz 20 grams of phenacyl bromide were dissolved in 100 grams of absolute alcohol. To this solution, cooled by means of a freezing mixture, a cold solution of 1.2 grams of sodium in 24 grams of absolute alcohol was gradually added. After remaining in the cold for an hour, the reaction mixture was poured into a large volume of water, and the 8-bromdiphenacyl filtered at the pump. Yield, 12 grams.

¹ Amer. Chem. J. 22, 25 (1899).

² Ann. 293, 70 (1896); Ber. 27, 1168 (1894).

³ Ber. 28, 3033 (1895); *ibid.* 29, 1750 (1896).

For the reduction of the 8-bromdiphenacyl 12 grams were dissolved in 600 grams of warm ninety-five percent alcohol, 30 grams of magnesium powder added and the mixture boiled under a reflux condenser for three hours. The solution was then filtered, the filtrate concentrated to one-third of its original volume and allowed to cool. The diphenacyl which separated was recrystallized from alcohol. Yield, about 6 grams. The yield was better by the latter method although the method of Knorr furnished a somewhat purer product.

2, 3-Dibenzoyl-5-nitrocyclopentadiene (I). $C_{19}H_{13}O_4N$.

To a solution of 1.6 grams of nitromalonic aldehyde and 0.8 gram (2 mols.) of sodium hydroxide in a mixture of 75 cc. of alcohol and 25 cc. of water, 2.4 grams of diphenacyl were added. The reaction mixture, in which the ketone is only slightly soluble, was kept at a temperature of 40° until homogeneous. The dark red solution was diluted with twice its volume of water, filtered, and acidified with dilute hydrochloric acid. The yellow, flocculent precipitate was filtered at the pump, washed with dilute alcohol, and crystallized from acetic ester. Yield, crude product, 75 percent of the theory. 2, 3-dibenzoyl-5-nitrocyclopentadiene crystallizes from acetic ester or acetone in yellow prisms which decompose at 237° - 238° . It is insoluble in water; only slightly soluble in alcohol, ether, acetic acid or ligroin; fairly soluble in benzene, chloroform, acetic ester or acetone.

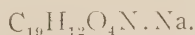
ANALYSIS.

0.1699 gram substance gave 0.4477 gram CO_2 and 0.0584 gram H_2O .

0.3710 gram substance gave 15.2 cc. moist nitrogen at 22° and 732 mm. pressure.

	CALCULATED FOR	FOUND
	$C_{19}H_{13}O_4N$	
C	71.48	71.85
H	4.08	3.85
N	4.40	4.45

Sodium salt of 2, 3-dibenzoyl-5-nitrocyclopentadiene (II).



The cyclopentadiene was treated with one equivalent of sodium dissolved in fifteen parts of alcohol. A little water was

then added in order to complete solution. Upon the addition of ether the yellow sodium salt was precipitated in crystalline condition. It is readily soluble in water, from which, by slow crystallization, it may be obtained in the form of thick needles. It crystallizes without water of crystallization.

ANALYSIS.

0.1800 gram salt gave 0.0373 gram Na_2SO_4 .

	CALCULATED FOR	FOUND
	$\text{C}_{19}\text{H}_{12}\text{O}_4\text{N} \cdot \text{Na}$	
Na	6.76	6.71

Barium salt of 2, 3-dibenzoyl-5-nitrocyclopentadiene.

The barium salt was prepared by the addition of barium chloride to a solution of the sodium salt in water. It is yellow in color, only slightly soluble in water, and crystallizes without water of crystallization.

ANALYSIS.

0.2293 gram salt gave 0.0698 gram BaSO_4 .

	CALCULATED FOR	FOUND
	$(\text{C}_{19}\text{H}_{12}\text{O}_4\text{N})_2\text{Ba}$	
Ba	17.77	17.92

Silver salt of 2, 3-dibenzoyl-5-nitrocyclopentadiene.

The cyclopentadiene was dissolved in dilute ammonia solution and the excess of ammonia removed by evaporation on the water bath. The solution was filtered, diluted and silver nitrate added. The silver salt came down as a yellow crystalline precipitate which was filtered at the pump and washed repeatedly with water. It is slightly soluble in water, and resembles the sodium salt in color. When heated it decomposes with explosive violence.

ANALYSIS.

0.1816 gram salt gave 0.0456 gram metallic silver.

	CALCULATED FOR	FOUND
	$\text{C}_{19}\text{H}_{12}\text{O}_4\text{N Ag}$	
Ag	25.33	25.11

Monoxime of 2, 3-dibenzoyl-5-nitrocyclopentadiene (III).



The condensation product (0.5 gram) was dissolved in a solution containing 0.52 gram of sodium hydroxide in a mixture of 15 cc. of alcohol and 15 cc. of water. After the addition of 0.44 gram (4 mols.) of hydroxylamine hydrochloride, dissolved in a little water, the mixture was kept at the boiling point for two hours. Upon acidification with hydrochloric acid a light yellow precipitate separated. After recrystallization from alcohol the pure product, melting with decomposition at 155° - 156° (corr.), was obtained. The oxime is readily soluble in benzene or chloroform; fairly soluble in ether, alcohol or carbon disulphide; soluble with difficulty in ligroin, and insoluble in water. From alcohol it crystallizes in slender yellow needles.

ANALYSIS.

0.1473 gram substance gave 0.368 gram CO_2 and 0.0567 gram H_2O .

0.1174 gram substance gave 9.2 cc. moist nitrogen at 23° and 737 mm. pressure.

	CALCULATED FOR	FOUND
	$\text{C}_{19}\text{H}_{14}\text{O}_4\text{N}_2$	
C	68.26	67.92
H	4.23	4.31
N	8.41	8.51

Monophenylhydrazone of 2, 3-dibenzoyl-5-nitrocyclopentadiene (IV). $\text{C}_{25}\text{H}_{19}\text{O}_3\text{N}_3$.

One gram of 2, 3-dibenzoyl-5-nitrocyclopentadiene was dissolved in three equivalents of warm sodium hydroxide solution (N/1) and treated with a warm solution of phenylhydrazine hydrochloride, in amount more than sufficient to neutralize all the alkali. The yellow, crystalline monophenylhydrazone, which came down in a short time, was filtered and washed thoroughly with water. It forms slender, yellow needles which are soluble in sodium hydroxide solution. The phenylhydrazone has no definite melting point since at a temperature of about 90° it is transformed into a pyridazine derivative with elimination of one molecule of water. This change occurs also when its solutions are warmed, and, for this reason, the substance cannot be recrystallized. For purification it was dissolved in alcohol and reprecipitated by the addition of a solution of sodium chloride. If the salt is not present in the solution the compound separates in a colloidal

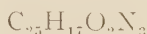
condition. The monophenylhydrazone is insoluble in water; slightly soluble in ligroin or acetic acid; fairly soluble in ether; readily soluble in alcohol, benzene, chloroform or carbon disulphide.

NITROGEN DETERMINATION.

0.1555 gram substance gave 15.1 cc. moist nitrogen at 24° and 728 mm. pressure.

	CALCULATED FOR	FOUND
	$C_{25}H_{19}O_3N_3$	
N	10.27	10.36

7-Nitro-1, 2, 4-triphenyl-cyclopentadio-dihydropyridazine(V).



As was indicated above, the monophenylhydrazone shows a marked tendency to pass over into a pyridazine derivative. When the preparation of this latter substance is the object in view it is not necessary, however, to first isolate the phenylhydrazone. Two grams of 2, 3-dibenzoyl-5-nitrocyclopentadiene were dissolved in hot benzene, two equivalents of phenylhydrazine added and the solution kept at its boiling point for ten hours. The mixture became dark red in color and in a short time began to deposit the pyridazine in the form of red, prismatic crystals. After one recrystallization from benzene a pure product, melting at 287° (corr.), was obtained.

7-nitro-1, 2, 4-triphenyl-cyclopentadio-dihydropyridazine is insoluble in sodium hydroxide solution and hence does not contain a hydrogen atom replaceable by metals. It is insoluble in alcohol, ether or ligroin; soluble with difficulty in chloroform or cold benzene; somewhat more readily soluble in hot benzene.

ANALYSIS.

0.1710 gram substance gave 0.4823 gram CO₂ and 0.0796 gram H₂O.

0.1850 gram substance gave 19.1 cc. moist nitrogen at 25° and 718 mm. pressure.

	CALCULATED FOR	FOUND
	$C_{25}H_{17}O_2N_3$	
C	76.73	76.91
H	4.40	5.18
N	10.76	10.81

Anil of 2, 3-dibenzoyl-5-nitrocyclopentadiene (VI).



To a cold, saturated solution of 2, 3-dibenzoyl-5-nitrocyclopentadiene in benzene five equivalents of aniline were added, the mixture heated on the water bath for half an hour and then allowed to stand at room temperature. In a few hours the anil began to separate out as a yellow, crystalline precipitate, and, after four days, the reaction had apparently gone to completion. The product was filtered and washed with benzene. For recrystallization it was dissolved in hot benzene and the solution treated with warm ligroin. The pure anil crystallized from the solution in the form of delicate, yellow needles which show a tendency to form aggregates. It is insoluble in water or ligroin; slightly soluble in alcohol or ether; fairly soluble in benzene, carbon disulphide, acetic acid, chloroform, acetone or acetic ester. The melting point is $264\text{--}265^\circ$ (corr.).

NITROGEN DETERMINATION.

0.1700 gram substance gave 11.1 c. moist nitrogen at 22° and 732 mm. pressure.

	CALCULATED FOR	FOUND
	$\text{C}_{25}\text{H}_{18}\text{O}_3\text{N}_2$	
N	7.11	7.08

OXIDATION OF 2, 3-DIBENZOYL-5-NITROCYCLOPENTADIENE.

A. WITH NITRIC ACID.

One gram of 2, 3-dibenzoyl-5-nitrocyclopentadiene, together with 40 c. of dilute nitric acid (sp. gr. 1.22), were placed in a 100 cc. flask, fitted with glass connections to a reflux condenser, and the mixture boiled until the substance had gone completely into solution. The presence of carbon dioxide among the products of oxidation was indicated by the formation of barium carbonate when the gases escaping from the top of the condenser were passed through a solution of barium hydroxide. The nitric acid solution was diluted, filtered, made alkaline with ammonia and then acidified with acetic acid. The addition of calcium

chloride produced a precipitate of calcium oxalate, showing that oxalic acid is formed in the process of oxidation. Benzoic and nitrobenzoic acids were also among the products.

Attempts to determine the amount of oxalic acid and carbon dioxide produced by the oxidation with nitric acid led to no satisfactory results, as the amounts of these substances formed appeared to vary between wide limits. In order therefore, to study the oxidation quantitatively the action of alkaline potassium permanganate solution on the cyclopentadiene was next investigated.

B. WITH POTASSIUM PERMANGANATE.

One gram of 2, 3-dibenzoyl-5-nitrocyclopentadiene was dissolved in 100 cc. of water containing four equivalents of potassium hydroxide, and the solution heated on the water-bath under a reflux condenser provided with a soda-lime exit tube. N/10 potassium permanganate was added in portions of 10 cc., the reaction mixture being kept alkaline by further additions of potassium hydroxide. In all, about 500 cc. of the permanganate solution were required. When the oxidation was complete a small amount of alcohol was added to destroy the excess of permanganate. The manganese dioxide was filtered and washed thoroughly with water. The filtrate was treated with an excess of ammonium chloride in order to remove the potassium hydroxide, and then a solution of calcium chloride added. The mixed precipitate of calcium oxalate and carbonate, which weighed 1.5634 grams, was dissolved in dilute sulphuric acid and the solution titrated with N/20 potassium permanganate, of which 114 cc. were required. This is equivalent to 0.3648 gram CaC_2O_4 . Subtracting this weight from the weight of mixed precipitate the weight of CaCO_3 is found to be 1.1986 grams.

The filtrate from the mixed oxalate and carbonate precipitate was made strongly alkaline with potassium hydroxide and evaporated to small bulk. After acidification with hydrochloric acid the solution was extracted repeatedly with ether. The ether was distilled and the residual benzoic acid purified by sublimation.

	CALCULATED	FOUND
CaC_2O_4 from 1 mol. oxalic acid	0.400	0.365
CaCO_3 from 3 mols carbon dioxide	0.940	1.198
2 mols. benzoic acid	0.764	0.737

The presence of nitric acid among the products of oxidation was revealed by the deep blue color produced when a solution of

diphenylamine in sulfuric acid was added to a portion of the filtrate from the manganese dioxide.

Attempts to reduce the cyclopentadiene derivative met with little success. Although acid reducing agents, such as various metals in conjunction with acids, and alkaline as well as neutral reducing agents were employed, it was found that either the substance was not reduced or that the reduction was accompanied by decomposition.

As already indicated 2, 3-dibenzoyl-5-nitrocyclopentadiene shows no tendency to form addition products. It was found that neither with the halogens, halogen acids, nor with benzoquinone, could the substance be involved in reactions analogous to those which characterize the parent substance of the group.

PARA-DIMETHYLDIPHENACYL AND NITROMALONIC ALDEHYDE.

The dimethyldiphenacyl required in this work was first described by Holleman⁴ and by Claus.⁵ For its preparation a modified form of Limpricht's method⁶ was used. One hundred and fifty grams of toluene and 25 grams of succinyl chloride were placed in a 500 cc. flask, provided with a reflux condenser, and treated gradually with 25 grams of aluminium chloride. The mixture was warmed to 50° on the water-bath for an hour and then allowed to remain at the ordinary temperature over night. The contents of the flask were treated with cold water, and the excess of toluene distilled with steam. The dark-colored, tarry residue, instead of being subjected to the fractional crystallization employed by Limpricht, was warmed with a slight excess of two percent sodium hydroxide solution. By this means the greater part of the tarry matter, as well as the lactone, is removed. The residual diketone was dissolved in hot alcohol and allowed to crystallize. After a second crystallization, with the aid of bone-black, a pure product was obtained. The yield was very poor, since the acid chloride reacts chiefly in the unsymmetrical form.

2, 3-*paraditoluyl*-5-nitrocyclopentadiene. $C_{21}H_{17}O_4N$.

To a solution consisting of 0.5 gram of sodium hydroxide, 1.0

⁴ Rec. trav. chim. 6, 76 (1887).

⁵ Ber. 20, 1377 (1887).

⁶ Ann. 312, 115 (1900).

gram of nitromalonic aldehyde, 15 cc. of water and 45 cc. of alcohol, were added 1.6 grams of succitolyketone. The mixture was kept at a temperature of 40° for 14 days, after which time the solution had acquired a deep-red color. About 25 per cent of the ketone remained unacted upon. An equal volume of water was added, the solution filtered and the filtrate acidified with dilute hydrochloric acid. The yield of the product, based on the unrecovered ketone, amounted to about 75 per cent of the theoretical. After recrystallization from acetic ester a pure product was obtained. 2, 3-paraditoluyl-5-nitrocyclopentadiene crystallizes in beautiful, yellow prisms which decompose at 243°-244° (corr.). It is insoluble in water; very slightly soluble in alcohol or ether; slightly soluble in glacial acetic acid or acetone; more readily soluble in benzene, chloroform or acetic ester. Besides acetic ester, glacial acetic acid may be used to advantage for the recrystallization of the substance.

ANALYSIS.

0.1642 gram substance gave 0.4372 gram CO₂ and 0.0794 gram H₂O.

0.2264 gram substance gave 8.7 cc. moist nitrogen at 21° and 734 mm.

CALCULATED FOR		FOUND
C ₂₁ H ₁₇ O ₄ N		
C	72.62	72.64
H	4.90	5.40
N	4.04	4.20

Silver salt of 2, 3-paraditoluyl-5-nitrocyclopentadiene.



The condensation product was dissolved in ten percent aqueous ammonia and, after the excess of the latter had been removed by evaporation on the water bath, the solution was diluted and filtered. Upon the addition of a solution of silver nitrate the silver salt was immediately precipitated. It is of a yellow color and only slightly soluble in water. When heated to a temperature of about 200° it is decomposed with explosive violence.

ANALYSIS.

0.1463 gram salt gave 0.0347 gram of metallic silver.

CALCULATED FOR		FOUND
$C_{21}H_{16}O_4N \cdot Ag$		
Ag	23.76	23.72

Monoxime of 2, 3-paraditoluyl-5-nitrocyclopentadiene.



One gram of 2, 3-paraditoluyl-5-nitrocyclopentadiene was dissolved in a solution containing 30 cc. of alcohol, 30 cc. of water, 0.8 gram of hydroxylamine hydrochloride and 1.0 gram of sodium hydroxide. The mixture was heated on the water-bath for four hours and then acidified with dilute hydrochloric acid. The oxime separated as a yellow, flocculent precipitate which was recrystallized from alcohol. It decomposes at a temperature of 150° - 151° (corr.). It is insoluble in water; slightly soluble in ligroin; fairly soluble in alcohol; readily soluble in ether, benzene or chloroform.

ANALYSIS.

0.1943 gram substance gave 13.6 cc. of moist nitrogen at 23° and 735 mm. pressure.

CALCULATED FOR		FOUND
$C_{21}H_{18}O_4N_2$		
N	7.73	7.58

4-BROMDIPHENACYL AND NITROMALONIC ALDEHYDE.

Para-bromacetophenone.

This substance was first described by Schweitzer⁷ who prepared it by the action of acetyl chloride upon brombenzene in carbon disulphide solution. Shortly afterwards Schöpf⁸ showed that the product was best purified by a steam distillation. In the light of the results of Perrier⁹ upon the most favorable conditions

⁷ Ber. 24, 550, (1891).

⁸ Ber. 24, 3766 (1891).

⁹ Ber. 33, 815 (1900).

for syntheses by means of the Friedel-Crafts reaction, the following procedure was adopted for the preparation of the ketone.

Seventy-six and one-half grams of aluminium chloride were placed in a 500 cc. flask and treated gradually with 50 grams of acetyl chloride. The mixture was warmed on the water-bath to complete the formation of the addition product, and then 90 grams of brombenzene in 150 cc. of carbon disulphide were poured gradually through the top of the condenser. The flask was heated on the water bath for six hours, after which time the evolution of hydrochloric acid had ceased. The excess of carbon disulphide was removed by distillation on the water bath, the residue poured upon cracked ice and finally subjected to a steam distillation. The ketone came over as an oil, solidifying completely in the receiver. The crude product was dissolved in hot alcohol and then hot water added to a slight, permanent turbidity. Upon cooling, the ketone separated as an oil, which, upon being stirred, was transformed into a mass of white crystals. The yield was about seventy per cent of the theoretical.

Perhaps, at this point, it may not be amiss to add a few words regarding the preparation of brombenzene. In the laboratory manuals of Gattermann, Sudborough and James, Henle and others, the procedures adopted furnish a yield of about sixty per cent of the theoretical. By following the method outlined below a yield of eighty to eighty-five per cent of pure brombenzene is easily obtained, while the amount of para-dibrombenzene is cut down to a minimum.

Into a 500 cc. distilling flask, whose side arm is bent upward at an angle of 45° and attached to a reflux condenser, 240 cc. of benzene and 4 grams of iron wire are placed. The flask is provided with a dropping funnel; and an exit tube leading from the top of the condenser serves to deliver the hydrogen bromide to a vessel containing water. One hundred cubic centimeters of bromine are now introduced into the benzene in the following manner: first, 5 or 10 cc. of bromine are added, and, when an evolution of hydrogen bromide is observed, the bromine is dropped in at such a rate that the temperature of the mixture rises slowly to 40° . A thermometer dipping into the solution serves to regulate the temperature, which should not be allowed to rise above this point; and, if the bromine be added in the proper manner, it will be found that the temperature can easily be maintained in the vicinity of this point, the evolution of hydrogen bromide becoming at no time tumultuous, but proceeding at an almost uniform rate. After all the bromine has been added, the flask is

maintained at a temperature of 40° until the evolution of hydrogen bromide has ceased. The product is now washed with water, dilute sodium hydroxide and again with water, separated and dried over fused calcium chloride. Fractionation, with the help of a Hempel column, should yield 240 grams of pure brombenzene, one or two grams of para-dibrombenzene remaining in the distillation flask. The recovered benzene may be used in another experiment.

Para-bromphenacyl bromide.

This substance has been described by Collet¹⁰ who prepared it by the action of bromine upon para-bromacetophenone in carbon disulphide solution, the solvent being subsequently evaporated in order to obtain the product. The compound was prepared by Collet also from bromacetyl chloride, brombenzene and aluminium chloride.¹¹ The following procedure was worked out, and gives an excellent yield of pure bromphenacyl bromide.

Twenty grams of para-bromacetophenone were dissolved in 80 cc. of glacial acetic acid, and to the solution 16.2 grams of bromine added. The flask was heated to 40° and the source of heat then removed. In a few minutes a vigorous reaction set in, the temperature rising spontaneously, the color due to the bromine disappearing rapidly, while copious fumes of hydrogen bromide were evolved. While yet hot the solution began to deposit the dibromketone in crystalline condition. The contents of the flask were heated on the water bath for ten minutes and then poured into 500 cc. of cold water. The product was filtered with the aid of suction, and recrystallized from ninety-five per cent alcohol. Yield, 25 grams, or ninety percent of the theoretical.

Para-bromphenacyl benzoylacetic ethyl ester (VII).



To a solution of sodium ethylate, obtained from 1.8 grams of metallic sodium and 35 cc. of absolute alcohol, 15 grams of benzoyl acetic ester were added. The alcoholic solution of the sodium salt of benzoylacetic ester, so obtained, was cooled, and then one equivalent, 21.7 grams, of para-bromphenacyl bromide added in four or five portions, the reaction mixture being shaken

¹⁰ Bull. Soc. Chim. (3) 21, 68 (1899).

¹¹ Comp. rend. 125, 718 (1897).

after each addition and cooled before treatment with the next portion. The flask became warm and sodium bromide was precipitated. The contents of the flask were then heated on the water bath for fifteen minutes in order to complete the reaction. Upon cooling, the product generally separated in crystalline form, although in one or two instances two liquid phases were present. The mixture was poured into cold water and the product filtered at the pump. After several crystallizations from alcohol the compound was obtained in the form of snow-white, delicate needles melting at 81° (corr.). The yield was about seventy-five per cent of the theoretical. By slow crystallization from ether, or a mixture of benzene and ligroin, the ester separates in beautifully crystalline condition: needles a centimeter or more in length. Para-bromphenacyl benzoylacetic ester is insoluble in water; fairly soluble in alcohol, ether or ligroin; readily soluble in carbon disulphide, acetic ester, acetone, chloroform or benzene.

BROMINE DETERMINATION.

0.2200 gram substance was taken for the determination of bromine by the sodium peroxide method.

CALCULATED FOR		FOUND
	$C_{19}H_{17}O_4Br$	
Br	20.55	20.63.

Para-bromdiphenacyl (VIII). $C_{16}H_{13}O_2Br$.

A solution of 6.8 grams (2 mols.) of potassium hydroxide in 150 cc. of water was introduced into a 500 cc. flask, provided with a reflux condenser; 50 cc. of alcohol and 20 grams of para-bromphenacyl benzoyl acetic ester were then added, and the mixture boiled for about three hours. At the end of this time the ester had gone completely into solution, and the diketone separated in the form of small crystals. The product was filtered off and recrystallized from alcohol. The yield was 7 grams or about 45 percent of the theoretical.

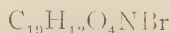
Para-bromdiphenacyl crystallizes in white plates of pearly lustre, closely resembling para-brombenzoic acid in appearance. Its melting point is 116° (corr.). It is insoluble in water; slightly soluble in cold alcohol, acetic acid or acetic ester; easily soluble in benzene, chloroform or hot alcohol.

BROMINE DETERMINATION.

0.2437 gram substance gave 0.1436 gram AgBr.

CALCULATED FOR		FOUND
$C_{16}H_{13}O_2Br$		
Br	25.21	25.08

2-Parabrombenzoyl-3-benzoyl-5-nitrocyclopentadiene.



The condensation of para-bromdiphenacyl with nitromalonic aldehyde is effected with relative ease. Into a solution made up of 45 cc. alcohol, 15 cc. of water, 0.5 gram (2 mols.) of sodium hydroxide and 1.0 gram of nitromalonic aldehyde, 2.0 grams of the diketone were introduced. The latter gradually went into solution, and, after the mixture had been maintained at 40° for five days, the reaction was complete, the ketone having entirely disappeared. The deep red reaction-mixture was diluted with twice its volume of water, filtered and acidified with dilute hydrochloric acid. The brown precipitate was filtered with the aid of suction, dried and purified by washing with acetic ester. Yield, about 75 percent of the theoretical. The pure product was obtained by recrystallization from benzene.

2-parabrombenzoyl-3-benzoyl-5-nitrocyclopentadiene crystallizes in small, yellow prisms which decompose at 240-241° (corr.). It is practically insoluble in water, ligroin, or acetic acid; only very slightly soluble in alcohol or ether; slightly soluble in acetone, carbon tetrachloride or acetic ester; fairly soluble in chloroform or benzene.

ANALYSIS.

0.1880 gram substance gave 0.3974 gram CO₂ and 0.0564 gram H₂O.

0.2078 gram substance gave 7.4 cc. moist nitrogen at 26° and 736 mm.

The bromine determination was made by Bacon's modification of Stepanow's method upon a 0.2170 gram sample.

$C_{19}H_{12}O_4NBr$		
C	57.28	57.64
H	3.04	3.34
N	3.52	3.83
Br	20.08	19.97

7-nitro-1, 2-diphenyl-4-*para*bromphenyl-cyclopentadio-dihydro-pyridazine, $C_{25}H_{16}O_2N_3Br$.

One gram of 2-*para*brombenzoyl-3-benzoyl-5-nitrocyclopentadiene was dissolved in hot benzene and three equivalents of phenylhydrazine added. The flask was heated on the water-bath for several hours and then an equal volume of alcohol was added to the red solution. Upon cooling, the solution deposited the pyridazine in beautiful, orange-red prisms, which, after recrystallization from benzene, showed a melting point of 246° (corr.).

7-nitro-1, 2-diphenyl-4-*para*bromphenyl-cyclopentadio-dihydropyridazine is insoluble in water; very slightly soluble in alcohol; slightly soluble in ether or glacial acetic acid; fairly soluble in acetone, carbon disulphide, benzene or acetic ester; more readily soluble in chloroform.

NITROGEN DETERMINATION.

0.1654 gram substance gave 14.2 cc. moist nitrogen at 25° and 734 mm. pressure.

	CALCULATED FOR	FOUND
	$C_{25}H_{16}O_2N_3Br$	
N	8.94	9.19

4, 4'-DIBROMDIPHENACYL AND NITROMALONIC ALDEHYDE.

Para-brombenzoic acid.

This acid appears to have been first prepared by Hübner, Ohly and Philipp¹² from *para*-bromtoluene by oxidation with chromic acid. A little later Fittig and König¹³ obtained the acid by the oxidation of *para*-bromethylbenzene with chromic acid. Schotten¹⁴ oxidized *para*-bromtoluene with nitric acid, while Weith and Landolt¹⁵ prepared the acid by a long series of reactions from *para*-bromdiphenylthiourea. By the action of bromine upon *para*-iodbenzoic acid Hirtz¹⁶ obtained *para*-brombenzoic acid. Beilstein recommends the oxidation of *para*-bromtoluene by means of chromic acid, as described by Jackson and Rolfe.¹⁷

¹² Ann. 143, 247 (1867).

¹³ Ann. 144, 283 (1867).

¹⁴ Ber. 21, 2248 (1888).

¹⁵ Ber. 8, 717 (1875).

¹⁶ Ber. 29, 1407 (1896).

¹⁷ Amer. Chem. J. 9, 84 (1887).

The method is, however, tedious, and the yield is rather poor. The following procedure was found to give better results:

Into a copper vessel were introduced 1500 cc. of water, 66 grams of para-bromtoluene and 55 grams of potassium permanganate. After boiling the mixture for about three hours under a reflux condenser the permanganate was completely reduced, and a second portion of 55 grams was then added. Again, after the reduction of this portion, the last 55 grams of permanganate was added and the mixture boiled until decolorized. The slight amount of bromtoluene remaining may be recovered by steam distillation, if desired. After the manganese dioxide had settled, the clear solution was poured through a filter, the dioxide boiled up twice with water, 400 cc. at a time, and filtered with the aid of suction. The washings were combined with the main filtrate and the whole evaporated in a porcelain dish to a volume of about 500 cc. After cooling, the calculated quantity of concentrated hydrochloric acid was added, and the para-brombenzoic acid filtered on a Büchner funnel. The yield amounted to about seventy percent of the theoretical.

Para-brombenzoyl chloride.

Raveill¹⁸ appears to have been the first to prepare this compound. Schotten¹⁹ describes it as distilling at 174° under 102 mm., while according to Sudborough²⁰ the substance boils at 154°-155° under 50 mm. pressure. Jackson and Rolfe²¹ obtained the acid chloride by a troublesome method involving crystallization from ligroin. The following method gave an excellent yield of pure product.

Thirty-five grams of para-brombenzoic acid were placed in a 500 cc. flask and treated with one equivalent of phosphorus pentachloride. The reaction was brought to completion by warming on the water-bath, and the products then separated by distillation under reduced pressure. In our work a pressure of 20 mm. was employed, and, after the phosphorus oxychloride had gone over, the whole of the acid chloride distilled at 135°-138°, solidifying completely in the receiver. The yield was ninety-two percent of the theoretical.

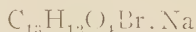
¹⁸ Ann. 222, 177 (1884).

¹⁹ Ber. 21, 2248 (1888).

²⁰ J. Chem. Soc. 67, 591 (1895).

²¹ Amer. Chem. J. 9, 85 (1887).

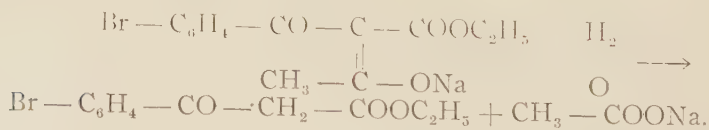
Sodium salt of para-brombenzoyl acetoacetic ester (IX).



A solution of sodium ethylate was prepared by dissolving 9.15 grams (2 mols.) of metallic sodium in 150 cc. absolute alcohol. Seventy-five cubic centimeters of this solution were put into a beaker, 25.8 grams (1 mol.) of acetoacetic ester added, and the solution cooled to 5°. Forty-two and eight-tenths grams (1 mol.) of para-brombenzoyl chloride were dissolved in 400 cc. absolute ether and one-half of this solution, 200 cc., added gradually from a burette to the solution of sodium acetoacetic ester, the temperature being maintained below 10°. The mixture was allowed to stand in the cold for half an hour, and, at the end of this time, 37.5 cc. of the sodium ethylate solution were added. One hundred cubic centimeters of the ether solution of the chloride were then run in as before, and, after the lapse of half an hour, 18.75 cc. of the sodium ethylate and 50 cc. of the ether solution were similarly added. In this manner, always using half of the remaining solutions, the experiment was continued until the whole of the sodium ethylate and acid chloride had been used up. The beaker was kept in a cold place for 24 hours when the separation of the yellow sodium salt, already begun after the second addition above, was complete. The product was filtered at the pump and washed with dry ether. A remarkable property of the sodium salt of parabrombenzoyl acetoacetic ester is its very slight solubility in water. The yield was 58 grams.

Para-brombenzoylacetic ethyl ester (X). $\text{C}_{11}\text{H}_{11}\text{O}_3\text{Br}$.

This ester was obtained from the sodium salt just described by gentle warming with aqueous ammonia. The reaction may be indicated as follows:



Fifty-eight grams of the sodium salt were suspended in 600 cc. water; 60 cc. concentrated ammonia water and 30 grams of ammonium chloride were added and the mixture maintained at a temperature of 40°-45° for about an hour, with constant shaking. In the course of this time almost the entire quantity of sodium salt had gone into solution and a heavy oil collected at

the bottom of the flask. The oil was removed by extraction with ether and the ethereal solution dried over calcium chloride. After distillation of the ether the residual oil was preserved in a vacuum dessicator over sulphuric acid for several days. The yield was 28 grams.

The bromine content of the ester was determined by Bacon's modification of Stepanow's method upon a sample weighing 0.3024 grams.

	CALCULATED FOR	FOUND
	$C_{11}H_{11}O_3Br$	
Br	29.49	29.32

Para-brombenzoyl acetic ethyl ester is a pale yellow, oily liquid, heavier than water, possessing a faint and not unpleasant odor. In dilute alcoholic solution the ester, in extremely small quantities, gives with ferric chloride a deep violet-red coloration—a test which is practically as delicate as that for ferric iron by ammonium sulphocyanate. Attempts to distil the ester, even at 5 mm. pressure, resulted in its decomposition. A considerable quantity of gas was evolved, and in the distillate the presence of alcohol and para-brombenzoic ester was detected. A yellow, granular solid, suspended in a brown, viscous liquid, remained in the distilling flask. The solid was freed from the greater part of the adhering impurities by washing with alcohol, and then recrystallized from glacial acetic acid. A bromine determination showed the substance to be dehydro-para-brombenzoyl-acetic acid. It is insoluble in water or ligroin; slightly soluble in alcohol, ether, acetone, chloroform, benzene, acetic ester or carbon disulphide; somewhat more soluble in glacial acetic acid. Its melting point is 261° (corr.).

	CALCULATED FOR	FOUND
	$C_{18}H_{10}O_4Br_2$	
Br	35.55	35.67

Para-bromphenacyl-para-brombenzoylacetic ethyl ester (XI).



To a solution of 1.7 grams (1 mol.) of metallic sodium in 35 cc. of absolute alcohol 20 grams of para-brombenzoylacetic ester were added. The alcoholic solution of sodium para-brombenzoyl-acetic ester was cooled and treated gradually with 20.6 grams (1

mol.) of para-bromphenacyl bromide. The solution became warm and separated into two liquid phases. To complete the reaction the flask was heated for a short time on the water-bath. The mixture was then poured into cold water, whereupon a heavy oil settled to the bottom. The product was extracted with ether, and the ether dried over calcium chloride. After the ether had been removed, the residual, dark-colored, viscous oil was preserved in a vacuum dessicator for several days. As the ester did not show any tendency to assume the solid form, a few cubic centimeters of alcohol were added and the mixture stirred until the contents of the dish had solidified to a yellow, crystalline mass. The product was dissolved in hot alcohol, and the solution treated with bone-black. Upon cooling, the concentrated, alcoholic solution deposited the ester as an oil which was gradually transformed into the solid. By crystallization from a dilute, alcoholic solution the ester may be obtained in the form of small, white prisms melting at 75° (corr.).

Para-bromphenacyl-para-brombenzoylacetic ethyl ester is insoluble in water; slightly soluble in ligroin or cold alcohol; fairly soluble in cold acetic acid or hot ligroin; readily soluble in hot alcohol; very soluble in ether, chloroform, acetone, benzene, carbon tetrachloride or acetic ester.

A bromine determination upon a sample weighing 0.2454 gram gave the following result:

CALCULATED FOR		FOUND
	$C_{19}H_{16}O_4Br_2$	
Br	34.16	34.36

4, 4'-Dibromdiphenacyl (XII). $C_{16}H_{12}O_2Br_2$.

Eight grams of para-bromphenacyl-para-brombenzoyl-acetic ester were boiled under a reflux condenser with a solution of 2.2 grams (2 mols.) of potassium hydroxide in a mixture of 40 cc. of water and 20 cc. of alcohol. The ester gradually went into solution, and soon the plate-like crystals of the diketone made their appearance. After the solution had been boiled for half an hour the reaction was complete. The product was filtered and recrystallized from benzene. Yield, about two grams, or thirty per cent of the theoretical.

4, 4'-dibromdiphenacyl crystallizes from benzene or glacial acetic acid in colorless, glistening plates, resembling monobromdiphenacyl in appearance, and melting at 182° (corr.). It is in-

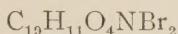
soluble in water; almost insoluble in ligroin; slightly soluble in alcohol, ether, or cold acetic acid; fairly soluble in benzene, acetone, or acetic ester; readily soluble in chloroform or hot glacial acetic acid.

BROMINE DETERMINATION.

A bromine determination upon a sample of substance weighing 0.2347 gram gave the following results:

	CALCULATED FOR	FOUND
	$C_{16}H_{12}O_2Br_2$	
Br	40.37	40.46

2, 3-para-dibromdibenzoyl-5-nitrocyclopentadiene.



In a mixture of 36 cc. of alcohol and 12 cc. of water 0.4 gram (2 mols.) of sodium hydroxide and 0.8 gram of nitromalonic aldehyde were dissolved; two grams of 4, 4'-dibromdiphenacyl were then added, and the solution maintained at a temperature of 40° for 14 ays. At the end of that time 60 per cent of the diketone had remained unacted upon and was recovered. After filtration the solution was acidified with dilute hydrochloric acid. The yellow precipitate was filtered off and recrystallized from a mixture of benzene and ligroin. The substance has no definite melting point but decomposes at 230°-232°.

2, 3-para-dibrombenzoyl-5-nitrocyclopentadiene is insoluble in water; slightly soluble in ether, alcohol, or ligroin; more readily soluble in benzene, chloroform or acetic ester.

ANALYSIS.

0.1889 gram substance gave 0.3340 gram CO_2 and 0.0426 gram H_2O .

0.2877 gram substance gave 8.4 cc. of moist nitrogen at 24° and 738 mm.

The bromine determination was made upon a sample weighing 0.1943 gram.

	CALCULATED FOR	FOUND
	$C_{19}H_{11}O_4NBr_2$	
C	47.80	47.97
H	2.33	2.51
N	2.94	3.17
Br	33.51	33.68

SUMMARY

We have shown by this research that the condensation of nitromalonic aldehyde with diphenacyl results in the formation of certain diketone derivatives of cyclopentadiene; that, possibly because of steric hindrance, only one of the two carbonyl groups of the condensation product can be made to react with hydroxylamine or aniline; that the monophenylhydrazone of the condensation product is readily transformed into a substance belonging to a new class of compounds to which the name *cyclopentadio-dihydro-pyridazine* is applied; and finally, that the rate of condensation with nitromalonic aldehyde increases in direct proportion to the increase in negativity of the substituent in the benzene nucleus of diphenacyl.

